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(54) Title: HIGH MOLECULAR WEIGHT POLYVINYLPYRROLIDONES AND METHOD FOR THEIR PREPARATION

(57) Abstract

An uncrosslinked, water-soluble polyvinylpyrrolidone having a K-value in excess of 120 and containing less than about 0.1 percent by weight of residual monomer. A method for preparing the high molecular weight polyvinylpyrrolidone is also disclosed.

HIGH MOLECULAR WEIGHT POLYVINYLPYRROLIDONES
AND METHOD FOR THEIR PREPARATION

BACKGROUND OF THE INVENTION

I.   Field of the Invention

The invention relates to a novel high molecular
weight water-soluble polyvinylpyrrolidone. In addition,
5   the invention relates to a novel method for the production
of water-soluble polyvinylpyrrolidones having a K-value of
from about 120 to 150.

II.   Background of the Invention

Polyvinylpyrrolidone is a well-known polymer
10   having numerous applications in the pharmaceutical,
cosmetic, agricultural, food, and other industries.
Various methods for its preparation from the monomer
N-vinyl-pyrrolidone are known. Normally, the polymeri-
zation is carried out either in aqueous solution or in
15   suspension in an organic or non-solvent in the present of a
free radical initiator.
One of the problems with solution polymerization
methods for the polymerization of N-vinyl-pyrrolidone is
that an upper limit of the molecular weight has become an

- 2 -

obstacle.   In particular, the solution polymerization processes known give commercially useful products having K-values of from about 10 to 90.   As used herein, the K-value is the so-called Fikentscher K-value which is obtained by

5   capillary viscometry utilizing the relative viscosity of a 0.1% w/v solution in water.   (See, U.S. Patent 4,190,718, columns 5 and 6.)   This K-value is related to the molecular weight of the polymer in a well-known manner and is conventionally used to characterize the molecular weight of poly-

10   vinylpyrrolidone.

One of the problems with the solution polymerization processes is that the viscosities of dilute aqueous solutions of polyvinylpyrrolidone products having K-values up to 90 are quite low.   For example, they normally are in

15   the range of less than 2 mPa.s in 2% aqueous solution.

For various uses, such as, thickeners, cosmetic formulations, printing inks, and the like, higher viscosities are required.   For example, other polymers, such as, polyacrylic acids in 1 to 3% solutions, exhibit

20   viscosities of 100 mPa.s.

Numerous attempts have been made to produce higher molecular weight polyvinylpyrrolidone which exhibits higher viscosities in aqueous solution.   Generally, these have used the crosslinking of polyvinylpyrrolidone using

25   crosslinking agents.   (See, for example, U.S. Patent 4,433,112.)   In this method, a starting material of poly-vinylpyrrolidone having a K-value of from 30 to 90 is treated by heating an aqueous solution of the polyvinylpyr-

- 3 -

rolidone in the presence of a water-insoluble organic
peroxide and the absence of air. Generally, these methods
start from an already polymerized polyvinylpyrrolidone.

5   The polymerization of N-vinylpyrrolidone in the
presence of a free radical initiator as well as the
mechanism of the polymerization is known. The polymeri-
zation consists of a sequence of four steps, namely, (1)
initiation; (2) propagation; (3) transfer; and (4) termina-
tion. In general terms, these steps may be depicted as
10   follows:

1. Initiation

$$I \longrightarrow R_d \longrightarrow 2R\cdot$$

$$R\cdot + M \longrightarrow M\cdot$$

2. Propagation

15

$$M\cdot + M \longrightarrow M - M\cdot \longrightarrow \longrightarrow M\cdot$$

3. Transfer

3a. To monomer

$$\longrightarrow M\cdot + M \longrightarrow P + M\cdot$$

3b. To polymer

20

$$\longrightarrow M\cdot + P \longrightarrow \longrightarrow M + \longrightarrow M\cdot$$

4. Termination

4a. Coupling

$$\longrightarrow M\cdot + \longrightarrow M\cdot \longrightarrow \longrightarrow M - M \longrightarrow$$

4b. Disproportionation

25

$$\longrightarrow M\cdot + \longrightarrow M\cdot \longrightarrow P + M \longrightarrow CH=CH_2$$

In the foregoing formulas, the symbols have the following
meanings:

- 4 -

R·   a radical from the free radical

            initiator

M   monomer

M·   radical monomer

—M·   polymerized monomer radical

P   polymer

—M-M—   higher molecular weight polymer

M—CH=CH$_2$ polymer with terminal unsaturation

As the polymerization proceeds and the amount of
higher molecular weight polymer concentration in the
reaction mixture increases, and the viscosity also
increases. The increased viscosity has the effect of
hampering the movement of the various moieties at their
various states of polymerization in the mixture. This, in
turn, decreases the possibility and the probability of the
individual entities in the mixture from coming together to
form additional polymer whether the entities are in the
radical form or the polymer form. In essence, the various
entities in the reaction mixture increasingly lose their
mobility due to the increased viscosity of the mixture.
Also, of course, for any given level of viscosity of the
mixture, the larger molecular weight moieties will always
have less mobility in the mixture than the lower molecular
weight moieties.

As a practical matter, this lack of mobility is
adverse to the propagation step but favors termination
making it difficult to obtain a product having a molecular

weight in excess of that represented by a K-value of

about 90.

SUMMARY OF THE INVENTION

We have discovered a novel water-soluble poly-

5   vinylpyrrolidone having a K-value in excess of 120 and con-

taining less than about 0.1% by weight of residual monomer

without crosslinking. We have further discovered that the

high molecular weight polyvinylpyrrolidone of the invention

may be prepared by subjecting a solution of N-vinylpyrroli-

10   done monomer in water to polymerization conditions utiliz-

ing a free radical initiator and adding water and initiator

to the reaction mixture incrementally in amounts and in

time periods during the polymerization so that the propa-

gation phase of the polymerization is maximized and the

15   termination phase is minimized by the control of the

process parameters. In addition, by adding a chelating

agent to the reaction mixture, we have found that it is

possible to minimize the residual amount of vinylpyrroli-

done monomer in the polymeric product.

20   The product obtained is highly useful since it is

not only of a high molecular weight, it exhibits excellent

solubility in water. As used herein, high or excellent

solubility means a solubility ratio of 5 as in accordance

with the description in Preparative Methods of Polymer

25   Chemistry; Sorenson and Campbell, Interscience, 1961;

p. 54.

- 6 -

Specifically, we have discovered that control of water and initiator addition allow one to control the individual phases of the polymerization so as to allow increased mobility of the reacting moieties and thus allow

5   the reaction to proceed to higher molecular weight final products than has heretofore been possible. By controlling the addition of water and making the addition of initiator incremental and spacing it over the course of the reaction, it is now possible to increase the propagation phase so as

10   to reach higher molecular weights.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Important control parameters for the inventive process are:

a)   The initial charge of initiator must be
15   accurately controlled and treated. Thus; it is
          best to maintain the initiator between about 30
          to 40°C until it is added to the reactive
          mixture. Also, the amount should be accurately
          measured to be within the ranges specified here-
20   in.

b)   The temperature should be controlled within the
          specified range herein throughout the reaction.
          While the reaction is exothermic, it proceeds
          relatively slowly; thus moderate cooling is re-
25   quired during the reaction.

c)   It is important to control the viscosity of the
          reaction mixture, particularly during the

- 7 -

reaction period from 4 to 7 hours after initia-
tion of the reaction. This is achieved by adding
water incrementally to maintain the viscosity
constant during this period. The constant vis-
cosity at this stage of the reaction permits
growth (propagation) of the molecular chains.

d)   Atmospheric environment must be kept inert, i.e.,
with a nitrogen or inert gas purge.

These parameters are discussed in detail herein-
below.

The initial reagents need not be purified,
although reactions have been carried out with N-vinylpyr-
rolidone which has been treated with activated carbon.
While the reaction rate is somewhat faster than those with
non-treated monomer, it is imperative that the monomer be
filtered to remove all traces of carbon, which otherwise,
can stop the reaction before high conversions are reached.

The initial concentration of monomer can have a
significant effect on obtaining the inventive product. The
initial monomer concentration should be kept in the range
from about 25 to 40% by weight based on the total weight of
water and monomer. If the initial monomer concentration is
below about 25% by weight, the inventive product is not
obtained in any useful yield. When the initial monomer
concentration is greater than about 40%, increased
agitation is required to achieve uniformity of the reaction
mixture because of the relatively high viscosity. The
greater agitation results in increased shear which produces

- 8 -

an undesirable shift in favor of the termination phase and
adverse to the propagation phase. Most preferably, we have
found that a monomer concentration of 27 to 28% by weight
is most desirable.

5   Of particular importance with the present inven-
tion is utilizing an incremental addition of the initiator,
i.e., adding the initiator to the reaction mixture more
than one time. This has the effect of maintaining the
reaction mixture viscosity uniform. It also increases the

10   initiator efficiency resulting in an increase in the
molecular weight of the vinyl product and a decrease in the
amount of residual monomer. Specifically, we have found
that the total amount of initiator added should be in at
least two separate additions, the first, initially to begin

15   the reaction, and the second at a later point in the
reaction. It is also possible to add the initiator in
three or four or more increments. We have found that two
or three increments is preferred.

          The total amount of initiator added generally is

20   in the range from about 0.01 to 2.0% by weight based on the
monomer and preferably, from about 0.1 to 0.2. The amount
added at each incremental addition would be an appropriate
half, third, or the like of the total amount to be added.

          The timing of the addition of the initiator may

25   be varied over the course of the total time period of the
reaction. Thus, if three additions are used (including the
initial addition of initiator), the second and third addi-
tions could be spaced at one-third intervals over the

entire course of the reaction. Similarly, the addition of
initiator when only two additions are made could be at the
half-time of the reaction. However, we have found in a
preferred embodiment that when two additions of initiator

5   are utilized (one in addition to the initial addition of
initiator), the second is made at approximately the three-
quarter point in the reaction.

　　　　　We have also found that the addition of a
buffering and chelating agent is critical in obtaining a

10   product with low residual monomer. This agent performs a
dual function in the reaction. Specifically, it complexes
with traces of heavy metals introduced by the aqueous
medium or by the reactor, which metals normally contaminate
the product and poison the catalytic initiator. The

15   buffering agent also controls the pH at a critical level of
not less than 5.5, preferably to a level on the basic side
between about 6.1 and about 10. Below a pH of 5.5 the
vinylpyrrolidone rate of polymerization is too slow to
compete with the more active quaternized comonomer. thus,

20   when the level approaches 5.5, additional quantities of
buffer are added to increase basicity. Generally, the
amount of buffer employed represents between about 0.01 to
0.5 weight %, preferably between about 0.04 to 0.3 weight %
of the vinylpyrrolidone monomer. Suitable agents which

25   combine buffering and chelating activity are those which
have a pH greater than 5 and include ethylene diamine
tetraacid disodium salt, tetrasodium pyrophosphate,
anhydrous dibasic sodium phosphate + monobasic potassium

- 10 -

phosphate, borax, sodium carbonate + sodium bicarbonate, tribasic sodium phosphate and calcium hydroxide. These buffering agents are employed as 0.005 molar to saturated aqueous solutions at 25°C. If the amount of buffer is too

5   great, the ash content of the product may increase beyond product specification. For example, for pharmaceutical end uses, the ash should be less than about 0.1% by weight. However, for non-pharmaceutical uses, higher ash contents can be tolerated, e.g., up to about 0.5% by weight.

10   However, if the amount of buffer is too low, the residual monomer content will be intolerable.

During the course of the polymerization, the viscosity of the reaction system increases. The viscosity can be measured in a variety of manners, e.g., torque mea-

15   surements and the like. Typical of such devices are the Heller HST-10 stir tester. We have discovered that by initiating the addition of water to the reaction mixture at a point in the reaction after a given amount of conversion to polymer has been achieved, and by adding this water in a

20   controlled manner, the viscosity of the reaction mixture can be maintained within a desired range of values so as to the propagation phase of the reaction and minimize the termination phase. This results in achieving the desired higher molecular weight product. Normally, the water is

25   added over a period of time at a constant feed rate with appropriate stirring to maintain the viscosity constant. While the addition of water may be started at various times during the reaction and continued for various periods of

time during the reaction, we have found that it is best to
add the water after a monomer conversion of from about 75
to 90% and preferably, from about 80 to 82%. This
corresponds to a reaction time of from about 210 to 240

5   minutes after the initiation of the reaction, when the
reaction is carried out at approximately 57-58°C.
Depending on the other parameters under which the reaction
is carried out, the time of addition of the water and the
period of addition over which the water is added can be

10   varied. What is important, however, is the discovery that
by the addition of water in this manner as well as the
variation of the other significant parameters as discussed
hereinabove, the propagation phase of the reaction can be
prolonged leading to higher molecular weight products.

15   Normally, the polymerization reaction is carried
out under an inert atmosphere. We have found that a
nitrogen purge is most desirable, although other inert
gases can be used.

            The temperature at which the reaction is carried

20   out does have an effect on the ultimate K-value of the
polymer. Also, understandably, the temperature has an
effect on the total time needed to carry out the reaction.
Lower temperatures would require a more prolonged reaction
time, whereas higher temperatures would lead to a shorter

25   and perhaps uncontrollable polymerization as well as
possible degradation of ingredients and/or product. We
have discovered that the preferred temperature range for

- 12 -

the reaction is from about 55 to 65°C and most preferably,
from about 57 to 60°C.

An important aspect of the invention is the con-
version of the product into a dry powder. Thus, for many
5   applications, the product must be redissolved in water and
generally, dissolution rate decreases with decreasing
particle size. Normally, this would be achieved by
removing the water from the reaction mixture and
pulverizing the product. However, care must be taken in
10   these final steps to avoid degradation of the product
(resulting in a decreased molecular weight). In parti-
cular, we have found that the most desirable procedure is
to utilize a drum dryer to produce the polymer in sheet
form. Alternatively, a belt dryer may be used. The sheet
15   is immediately passed through a pin shredder to break it
into flakes and flakes are then ground to a desired powder
size. Particularly important in this procedure is that the
product solution be dried as soon as possible after the
reaction is complete to avoid any detrimental change in the
20   product.

In particular, using either drum or belt drying,
a product having a water content below about 4.5 weight
percent without any K-value degradation is obtained the
drying temperature is generally in the range from about 250
25   to 260°C for belt drying and about 290 to 330°C for drum
drying.

The dried product is then ground in a manner to
minimize K-value degradation. While a variety of grinding

devices may be used, we have found a Fitzmill to be parti-
cularly satisfactory. In particular, acceptable powder was
produced using a Fitzmill with a 0.094 inch screen and
rotor speed of 3600 rpm. the desirable product is in the
5   form of a powder of which 80% is between 16 and 40 mesh and
less than 10% passes a 40 mesh screen (U.S. Standard).

The following example illustrates the present
invention:

For this reaction, a 12 liter reactor equipped
10   with a condenser, an anchor agitator with a speed/torque
readout, a thermocouple, a nitrogen inlet, and a dropping
funnel were utilized. All of the reagents were used
without purification. Nitrogen was bubbled through the
reaction mixture during the entire course of the reaction.
15   4,541 grams of deionized water and 1.69 grams of
tetrasodium pyrophosphate were added to the reactor and
mixed at 110 rpm for 5 minutes. The agitation was stopped
and then 1,687 grams of vinylpyrrolidone were added after
it was assured that the tetrasodium phosphate had been
20   completely diluted. The agitator was again turned on and
maintained at approximately 110 rpm. A nitrogen purge was
initiated through the reaction mixture. The reaction
mixture was heated to and held at a temperature of 53-54°C
and then 1.67 grams of t-butylperoxypivalate was added.
25   This time was taken as time zero. Any residual initiator
clinging to the sides was washed from the interior of the
reactor with a small amount of water. The reaction
exotherm brought the temperature into the range of from

- 14 -

about 57 to 60°C. This temperature range was maintained during the next 420 minutes of the reaction. Neither heating nor cooling was required to maintain the temperature. (If needed, heat may be supplied at approximately

5   57.5°C and terminated at 58.5°C to maintain the reaction temperature uniform.)

     After 210 minutes, the addition of deionized water was begun at a feed rate of 10.4 grams per minute. The total amount of water added in this manner was 2,187

10   grams so that the feed was completed after a reaction time of 420 minutes (a total feed time of 210 minutes). The water was added continuously using a dropping funnel. The addition rate of water was monitored by measuring the torque of the polymerization mixture. In this example, the

15   agitator was set at 110 rpm and the torque was maintained to at least the value observed at 210 minutes.

     At this point, the conversion of monomer was about 80 to 82%. The reaction mixture had a Brookfield viscosity of 40,000 cps at 57°C, and the K-value of the

20   polymer was 105 ± 2. The torque was 14.5 oz-inch.

     At 330 minutes, a second addition of t-butylperoxypivalate (1.77 grams) was effected and any residual initiator washed from the inside of the flask with a small amount of water. At this point, the conversion was between

25   85 and 87%. This second amount of initiator was added at a time when the concentration of monomer and polymer was 23% by weight.

- 15 -

At 420 minutes, the polymerization was terminated by heating the reaction mixture to 80 ± 2°C within a period of 15 minutes and holding it at this temperature for an additional 15 minutes to thus polymerize remaining monomer.

5   At this point, the conversion of the monomer was 98 to 99.5%, and the concentration of polymer/monomer about 20%. At 450 minutes, the reaction was terminated by turning off the nitrogen purge and cooling the reactor. The reactor was discharged at 55-60°C, the residual monomer of the

10   polymer product in aqueous solution was less than 0.2% which is the limit of detection and the K-value of the polymer was 119-125.

A series of polymerizations were carried out in glass wherein the amount of chelating and buffering used

15   (tetrasodium phosphate) was varied with the remaining reaction parameters being the same as described above. The results are depicted in the Table. As shown therein, while it is possible to achieve K-values greater than 120 even in the absence of the chelating agent, the percent of residual

20   vinylpyrrolidone monomer is extremely high (0.23%). In contrast, with even a relatively small amount of the TSPP, (0.01 weight %), the residual monomer is minimized.

For the results tabulated in the Table, the residue on ignition and residual vinylpyrrolidone monomer

25   were determined as follows:

<u>Residue on Ignition</u>

10 g of sample were weighed in a crucible that had previously been ignited, cooled, and weighed. The

- 16 -

crucible was heated gently at first until the sample was thoroughly charred. It was then cooled and the residue moistened with 2.0 ml (1:1) of sulfuric acid and heated gently until white fumes no longer evolved. The sample was then ignited at 800°C ± 25°C until the carbon was consumed. It was cooled in a desiccator, weighed and the ash content was calculated as follows:

$$\% \text{ ash} = \frac{W_2 - W_0}{W_1 - W_0} \; 100$$

wherein W_0 = crucible weight
W_1 = sample and crucible before ashing
W_2 = sample and crucible after ashing

Determination of Percent Vinylpyrrolidone

A sample was weighed into a 250 ml Erlenmeyer flask, the sample was dissolved in 10 - 20 ml of distilled water or reagent grade alcohol as required. 10 ml of 5% sodium acetate is added. If the solution is cloudy, reagent alcohol is added until the solution clears. The contents are mixed well and then titrated with a 0.1 N iodine solution until a straw color appears. An additional 5 ml of the iodine solution is added. The total amount of iodine added is recorded.

The flask is swirled and set aside for 5 minutes. If the color disappears at the end of this time, 3 additional ml of iodine are added and the contents are allowed to stand for 3 minutes. The amount of iodine of additional iodine solution added is recorded.

- 17 -

The solution is then titrated with 0.1 normal sodium thiosulfate until it is a light yellow. 5 ml of starch indicator is added. If alcohol is used as a solvent, the solution should be titrated without the starch

5 because starch gives a poor endpoint. The titration is continued until a sharp colorless endpoint is obtained.

The percent vinylpyrrolidone is then calculated using the following formulas

1.

$$\% \text{ VP} = \frac{[(ml_1 \times N_1) - (ml_{thio} \times N_{thio})]\ 5.555}{g\ sample}$$

10

2.

$$\% \text{ VP} = \frac{[(ml_1 \times N_1) - (ml_{thio} \times N_{thio})]\ 555.5}{g\ sample \times \%\ solids}$$

TABLE 1

Run No.	Wt. % TSPP On Wt. VP	% Solids	Residue on Ignition (On 100% Solids)	K-Value 0.1% Water	10% Soln % VP	pH As Is	pH 5% Soln
1	0.10	10.4	0.13	138	0.04	7.60	6.68
2	0.05	10.4	0.05	137	0.06	6.85	6.42
3	0.01	10.3	<0.03	137	0.05	6.75	6.38
4	0.00	10.9	<0.01	122	0.23	6.20	5.61

WHAT IS CLAIMED IS:

1.   Polyvinylpyrrolidone which is water-soluble
and non-crosslinked, has a K-value in the range from about
120 to 150, and a residual monomer content of less than
about 0.1 percent by weight.

2.   The polyvinylpyrrolidone of claim 1 in the
form of a dry powder.

3.   The polyvinylpyrrolidone of claim 2 wherein
about 80% of the powder is between about 16 and 40 mesh and
less than about 10% is less than 40 mesh.

4.   The polyvinylpyrrolidone of claim 3 having a
water content of less than about 4.5%.

5.   A method for producing the polyvinylpyrroli-
done of claim 1 comprising the steps of:
    a)   forming a mixture of N-vinylpyrrolidone
          monomer, a chelating buffer, and water;
    b)   subjecting the reaction mixture to
          polymerization conditions in the presence of
          an initiator for a period of time to convert
          substantially all of the monomer to
          polyvinylpyrrolidone;

    c)   during the polymerization, maintaining the viscosity of the reaction mixture sufficiently constant so as to maximize the propagation phase and minimize the termination phase of the polymerization.

6.   The method of claim 5 wherein the initial reaction mixture contains from about 25 to 40 percent by weight monomer based on the weight of water and from about 0.05 to 0.5 weight % of chelating buffer.

7.   The method of claim 5 wherein the polymerization is carried out at a temperature in the range from about 55 to 65°C.

8.   The method of claim 1 wherein the viscosity is kept constant by the incremental addition of water and initiator to the reaction mixture.
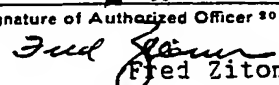
9.   The method of claim 5 wherein after termination of the reaction, the product is dried in a belt or drum dryer and the dried product is ground to a powder of which about 80% is between 16 and 40 mesh and less than about 10% is less than 40 mesh.

10.   The method of claim 9 wherein the product is dried to a water content of less than about 4.5%.

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 3

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C08F 26/08, 26/10, 22/38; A61K 31/79

U.S. CL: 526/264, 263, 258; 525/326.7, 326.8; 424/80

II. FIELDS SEARCHED

Minimum Documentation Searched 4

Classification System	Classification Symbols
U.S.	526/258, 260, 264 424/80 525/326.7, 326.8, 326.9

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched 5

III. DOCUMENTS CONSIDERED TO BE RELEVANT 14

Category *	Citation of Document, 16 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 18
X Y	US, A, 3,862,915 (FRIED) 28 JANUARY 1975; See entire document.	1, 5-8 2-4, 9, 10
Y	US, A, 4,058,655 (DENZINGER) 15 NOVEMBER 1977; See Column 4, lines 4-30.	2-4, 9, 10
Y	US, A, 4,190,718 (LORENZ) 26 FEBRUARY 1980; See Column 2, line 47 and Column 7, line 36.	2-4, 9, 10
A	US, A, 4,554,311 (BARABAS) 19 NOVEMBER 1985; See entire document.	1-10
A	US, A, 4,433,112 (STRAUB) 21 FEBRUARY 1984; See entire document.	1-10
A	US, A, 4,053,696 (HERRLE) 11 OCTOBER 1977; See entire document.	1-10

* Special categories of cited documents: 15

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 2	Date of Mailing of this International Search Report 2
02 MAY 1991	05 JUN 1991
International Searching Authority 1	Signature of Authorized Officer 20
ISA/US	Fred Zitomer

Form PCT/ISA/210 (second sheet) (May 1986)

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